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Sputtering of NiTi alloys: a comparison of experiment and simulation

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Polycrystalline alloys have been sputtered using a 4 keV Ar⁺ ion beam. The experiment has been modelled using different computer simulation techniques—static and dynamic Monte Carlo simulation, and a binary collision lattice code. A comparison between the results of the experiment and the simulations and among the different computer programs has been made. These are also compared with the predictions of the linear cascade theory. The relative importance of the surface binding energy, of the depth of origin and of the modified steady-state surface composition on the observed angular dependence of the deposit composition are assessed.

1. Introduction

Investigations of the sputtering of multi-component targets contribute to the improved understanding of the processes which take place during the bombardment of solids by accelerated ions. It should be noted that in all cases (except self-sputtering), after a certain ion fluence the target becomes in effect multi-component due to the incorporation of the primaries.

As shown previously, the angular distributions of the sputtered target components may vary with the polar angle of ejection¹⁻⁷. This is due to the unequal transfer of the projectiles' energy to the different target species⁸. This leads to preferential sputtering of one of the components, thus creating a concentration gradient near the surface which, in turn, causes differences in the angular distributions of the different sputtered species⁹.

The main purpose of the present work is to investigate the sputtering phenomena during Ar⁺ ion bombardment of NiTi polycrystalline alloys and especially the angular distributions of the sputtered components via computer modelling with different binary collision computer codes (static TRIM^{10,11}, MARLOWE^{12,13} and dynamic TRIM¹⁴).

2. Experimental

The measurements were carried out in an experimental set-up which has been described in detail elsewhere¹⁵. An ion gun of the duoplasmatron type was used. A mass-separated primary ion beam was incident along the normal to the surface with a beam current I_p typically 20 μ A and a diameter $\phi = 2$ mm.

The sputtered flux was collected on a semi-cylindrical Al foil with a radius $R = 30$ mm. The operating pressure in the target chamber was 1×10^{-7} torr. Prior to deposition, the target was sputtered onto a shutter until steady-state was reached. The composition of the collected material was analysed by Rutherford backscattering spectroscopy (RBS).

The experimental results on the angular distributions of sputtered neutral particles from NiTi alloys are given in ref 7. The Ti polar angular distribution is found to be wider than that of Ni, the latter being emitted preferentially closer to the surface normal. The dependence of the Ni/Ti ratio on the polar angle of ejection θ is shown in Figure 1. The distribution is normalized to

1 at $\theta = 45^\circ$ because it was found that the composition of the sputtered flux along that direction corresponded to the bulk stoichiometry. This observation is in agreement with the results obtained in ref 16.

3. Simulation results

It is generally accepted that simulation by bombardment of virgin surfaces is only valid for very low primary ion beam doses. In the case of multi-component targets, simulation is usually performed with a surface concentration equal to the bulk concentration, i.e. the concentration gradients possibly existing prior to the bombardment and due to, e.g. Gibbsian segregation are not taken into account.

The experimental results were obtained in a steady-state regime, i.e. far away from a low fluence regime. We decided initially to explore the suitability of the most widely used computer codes for investigating the polar angle distributions of the

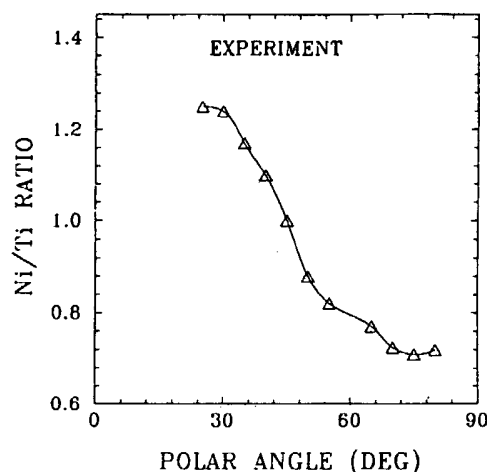


Figure 1. Ratio of sputtered Ni and Ti atoms as a function of polar angle of ejection. Experimental data from RBS analysis of material sputter deposited onto a semi-cylindrical Al collector⁷.

components sputtered from virgin NiTi alloys. These are the MARLOWE binary collision lattice code and the static TRIM code.

3.1. MARLOWE computer simulation. A modification¹⁷ of MARLOWE version 12 (refs 12 and 13) was used for the simulation. Since the program treats crystal structures, we have introduced the B2 (CsCl type) crystal structure for the NiTi alloy with a lattice constant 3.07 Å (ref 18). The program was run in its polycrystalline mode. The Molière interatomic potential with default screening lengths was used. Since molecular dynamics (MD) simulations have showed an energy loss of some tenths of electronvolts in the case of energy transfer by focusons¹⁹, we have introduced a replacement energy of 0.2 eV. The displacement energies were chosen at 5 and 3 eV for Ti and Ni, respectively, following the recommendations of ref 20. The cut-off energies were set equal to the surface binding energies for which the energies of sublimation of the pure elements were used, 4.44 and 4.89 eV for Ni and Ti, respectively²¹. The particles ejected along a given polar angle are integrated for all azimuthal directions as the incident ion beam direction is along the surface normal and the target is polycrystalline. The simulated ratio of the sputtered Ni and Ti atoms vs the polar angle of ejection for all azimuths and all energies is shown in Figure 2(A). Slight preferential ejection of Ni atoms along the surface normal is observed. The slope of the curve is less pronounced than that of the experimental one.

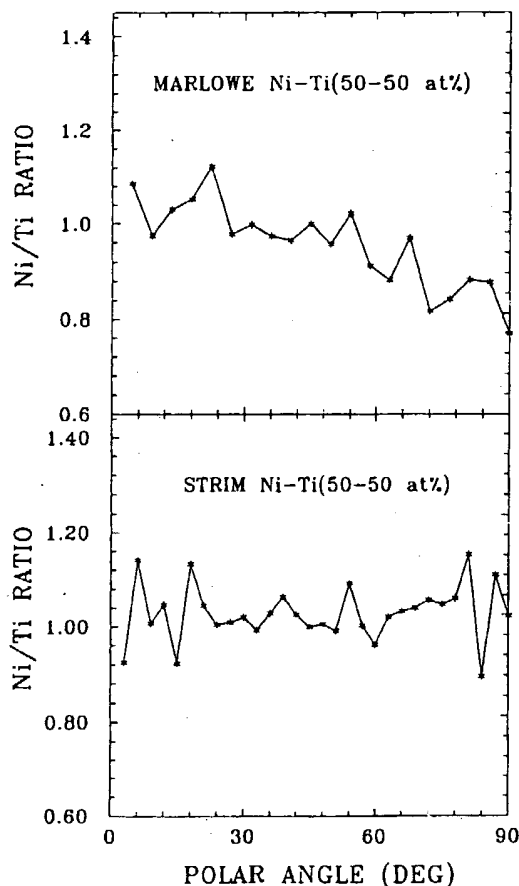


Figure 2. Simulated ratio of sputtered Ni and Ti atoms as a function of polar angle of ejection: (A) MARLOWE; and (B) static TRIM.

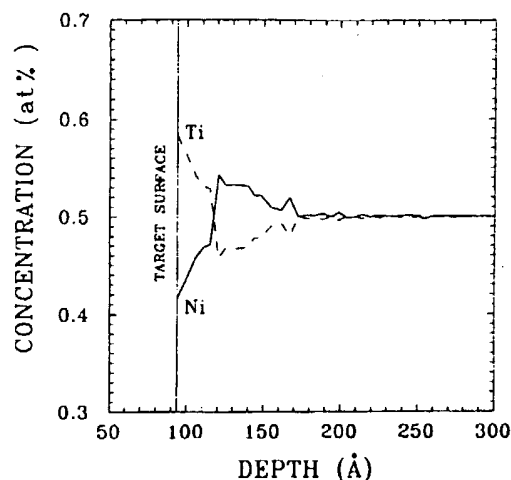


Figure 3. Simulated depth concentration profiles of Ni and Ti after 4 keV Ar⁺ bombardment to a dose of $3.5 \times 10^{16} \text{ cm}^{-2}$ (steady-state).

3.2. TRIM computer simulation. A standard three-dimensional TRIM^{10,11} computer code with a modified subroutine for producing the angular distributions of the sputtered particles is used for this simulation. The angular distributions are corrected for the solid angle seen by the detector. The input data are the same as used for the MARLOWE simulations. The results of these calculations are shown in Figure 2(B). The Ni/Ti ratio vs polar angle of ejection shows no preferential sputtering directions for any of the components. It is difficult to explain the differences in the predictions of MARLOWE and TRIM.CASC since the only differences in the input are that the former treats a polycrystalline target, whereas the latter deals with a random one.

3.3. Dynamic TRIM computer simulation. It is clear that concentration changes near the target surface strongly influence the angular distributions of the sputtered constituents. We used a dynamic TRIM code¹⁴ to obtain the steady-state surface concentrations and the concentration gradients in the near surface region. The input parameters such as surface binding energy, bulk binding energy, cut-off energy, etc. were chosen the same as with the static computer calculations. The dose necessary for reaching steady-state was found to be about $1 \times 10^{16} \text{ cm}^{-2}$. The presented data were collected for the dose interval between 2 and $4 \times 10^{16} \text{ cm}^{-2}$ by simulating 20,000 pseudoprojectiles. The change of the target concentration as a function of depth in steady-state sputtering conditions is shown in Figure 3. The enrichment of Ti on the surface is in agreement with the results of ref 22.

We have used the additional subroutine for extracting the particle ejection distributions of the constituents. The obtained Ni/Ti ratio vs the polar angle of ejection is shown in Figure 4(A). The results are an improvement over the predictions of the static TRIM, however, the values again vary between smaller limits than the experimentally obtained ones. The possible reasons for this are discussed further below.

3.4. Linear cascade theory calculations. The cascade theory of sputtering^{9,23} provides expressions for the differential yield as a function of emission energy (E), polar angle of emission (θ), and depth of origin (x).

A computer program for calculating the angular distributions

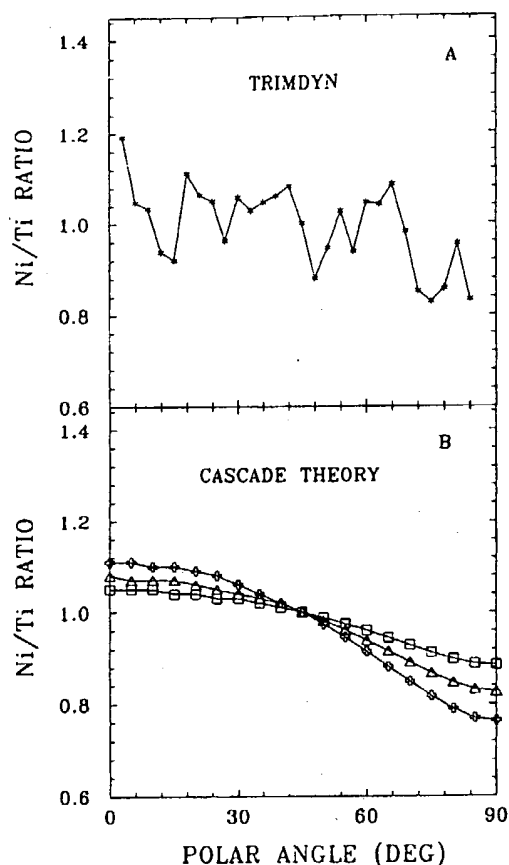


Figure 4. Calculated ratio of sputtered Ni and Ti atoms as a function of polar angle of ejection: (A) dynamic TRIM: (B) following the model of refs 9 and 23: (□)— $K = 2$, (△)— $K = 3$, (+)— $K = 5$. $A_0\lambda = 0.5$ in all cases.

of the sputtered components⁷ based on the linear cascade theory was used for simulating the sputtering of NiTi alloys. The program uses, as independent input parameters, the characteristic depth of sputtering (A_0) and the coefficient of bombardment-induced segregation K defined as the ratio of $x_{A(2)}^\infty/x_{B(2)}^\infty$ to $x_{A(2')}^\infty/x_{B(2')}^\infty$. Here $x_{i(2)}^\infty$ and $x_{i(2')}^\infty$ represent the concentrations of the elements ($i = A, B$) at steady-state (∞) on the surface (2) and in the region where the bombardment-induced segregation ceases (2') following the notation adopted in ref 23. Imposing $A_0\lambda = 0.5$, where λ is the mean atomic spacing and assigning different values to the bombardment-induced segregation parameter K , we obtain the results shown in Figure 4(B) which exhibit the same trend as the experimental data. Very high values of K are necessary in order to fit the calculation to the experiment reasonably well.

4. Discussion

The results indicate that these types of experiments cannot be modelled adequately using standard unfitted input parameters in the simulations.

There are basically two reasons for the different angular distributions of the species sputtered from multi-component targets. One is related to the different concentration gradients of the components in the near-surface region. Let us assume that in the cascade all types of recoiling atoms receive randomly oriented

momenta. Thus, atoms ejected from the outermost monolayer will have a wider angular distributions compared with that of atoms being sputtered from deeper target layers. This means that the component with the higher surface concentration will have the wider angular distribution. The other major reason for the differences in angular distributions are the different surface binding energies of the target components. Since sputtered particles have to overcome a planar surface barrier in order to become free, their trajectories are in effect refracted away from the normal. Thus, the atoms with the higher surface binding energy will have a higher probability of being ejected closer to the surface.

These considerations indicate the most evident means of adjusting the parameters of the simulations to achieve better agreement with the experiment. In effect, the influence of radiation-induced segregation on the angular distributions of Ni and Ti is seen in the predictions of the cascade theory calculation, cf. Figure 4(B).

Thus, one possibility of improving the correspondence of the static simulation results to the experimental data would be to place a thin overlayer which reflects the changed surface composition in steady-state. Helpful information is contained in the simulated depth profiles of the component concentrations, cf. Figure 3, although the changes there occur over larger distances. It should be noted that dynamic TRIM does not contain mechanisms producing segregation and the modelled target modification is due solely to ballistic effects. The dynamic TRIM simulation indicates a surface composition corresponding approximately to $Ni_{1.2}Ti_3$. In order to introduce such an overlayer in MARLOWE, we constructed a crystal structure with this composition and a lattice constant of 5.16 Å obtained from the calculated density of $Ni_{1.2}Ti_3$. The presence of such an overlayer on top of the NiTi substrate does not lead to improved agreement with the experiment. Moreover, various attempts to account for the modified surface concentration in static TRIM also did not produce noticeable improvement. These attempts included bombarding a semi-infinite $Ni_{0.4}Ti_{0.6}$ target, a semi-infinite $Ni_{0.5}Ti_{0.5}$ with a 5.16 Å overlayer of $Ni_{0.4}Ti_{0.6}$ and a semi-infinite $Ni_{0.5}Ti_{0.5}$ with a monolayer of $Ni_{0.4}Ti_{0.6}$.

Our results indicate that accounting only for the change in surface composition by placing an overlayer on top of a substrate with bulk composition does not necessarily lead to a better fit to the experiment. Apparently, the concentration gradient introduced in this manner is not sufficient to produce the significant differences in the angular distributions of the sputtered components.

The other obvious possibility of fitting the experiment would be increasing the difference in the surface barriers of the components. One justification for this could be the presence of oxygen on the target surface. Since Ti-to-O bonding is stronger than Ni-to-O, it may be assumed that TiO forms on the surface, thus increasing the surface binding energy for the Ti. Such a change of the surface binding energy will lead to greater refraction of the sputtered Ti atoms towards the surface which will broaden the Ti angular distribution, although it will also lead to lowering of the Ti partial sputtering yield. Oxygen presence may also produce chemically enhanced segregation of Ti on the surface.

5. Conclusions

The angular distributions of the species sputtered from polycrystalline NiTi targets have been modelled using the most wide-

spread computer simulation programs with standard values of the input parameters. The results of such MARLOWE, dynamic TRIM and cascade theory calculations exhibit the same qualitative trend as the experimental data. Simple descriptions of the modified surface composition by placing overlayers on top of an unchanged target did not lead to noticeable differences in the angular distributions of the components. Further investigations of the influence of the depth of origin and the concentration gradients in the sub-surface region are necessary. Better agreement with experiment may be obtained by adopting physically reasonable values of input parameters which are different from the default ones.

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